

Reaction Characteristics During *In-Situ* Gasification of Western Subbituminous Coals

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INTRODUCTION

In-situ gasification of coal offers a number of significant potential advantages which suggest its use both as a supplement to and, in some cases a substitute for conventional mining combined with surface gasification. These include:

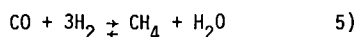
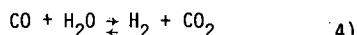
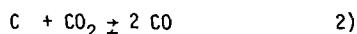
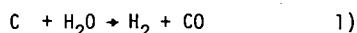
- Utilization of coal reserves which cannot be economically recovered by conventional techniques
- Reduction of capital expenditures and operating costs
- Easier and more economic control of pollution problems
- Less stringent feed water quality requirements
- Reduction of the health and safety problems associated with conventional coal processing techniques
- Reduction of socioeconomic impact

In underground gasification, wells are drilled into a coal seam for gas injection and product recovery and are linked by means of any of several techniques including: reverse combustion, hydrofracturing, electro-linking, directional drilling, and explosive fracturing. The linking step facilitates movement of product gas from the reaction zone to the recovery wells.

Maintenance of a high-permeability link between wells is extremely difficult with Eastern coking coals, because of their swelling at high temperatures. In addition, transport of water and reactant gases through Eastern seams is more difficult because of the lower permeability of the coal itself in its natural state. As a result, the greatest success has been with underground gasification of Western subbituminous coals and Texas lignites.

Field studies are currently being carried out by the Morgantown Energy Research Center with Pittsburgh seam coal near Pricetown, West Virginia, but no complete gasification test has yet been completed. Several gasification tests have been completed by the Laramie Energy Research Center at Hanna, Wyoming, and by Lawrence Livermore Laboratory at Hoe Creek, Wyoming. In addition, Texas Utilities Service Company has conducted field tests in Texas lignite deposits, utilizing technology licensed from the Soviet Union.

In underground coal gasification (UCG), three more-or-less well-defined reaction zones can be identified. The zone nearest the product recovery well is the drying and pyrolysis zone, in which water is driven from the coal and the pyrolysis reactions occur. Tars produced in this zone are continually driven forward into the cooler regions of the seam, with a portion being cracked to lighter hydrocarbons. Cracking proceeds until the tars are light enough to be carried with the product gas stream out of the coal seam. Immediately behind the pyrolysis zone is the reducing zone or gasification zone. In this area, the primary reactions are:



The water necessary for reaction 1) is supplied either by injection of steam with the air or oxygen or by natural intrusion of water into the reaction zone if the coal seam is a natural aquifer (as is the case for many Western coal seams). Behind the gasification zone is the combustion zone, which supplies the process heat. Heat is transferred from the combustion zone to the gasification zones primarily by convection of the product gases, rather than by conduction through the solid char and coal.

In experimental studies at Argonne, the kinetics of the reactions occurring in the gasification zone are being measured. The data from these studies are used in mathematical models being developed at other laboratories for each of the field projects. This paper describes the reaction characteristics of coals from the Hanna No. 1 and Wyodak coal seams for reactions 1), 4), and 5). Data for reactions 2) and 3) are not yet complete and are not discussed here.

EXPERIMENTAL

The kinetic experiments were carried out in a differential packed-bed reactor system capable of simulating any of the operating conditions expected in underground gasification. A schematic of this system is shown in Fig 1. The product gas from the reactor is analyzed for H_2 , CO , CH_4 , and CO_2 by gas chromatography. All operating temperatures, pressures, and gas flows are monitored and recorded on punched paper tape by means of a data logging system. In addition, the data output from the gas chromatograph is recorded on punched tape, permitting rapid computer processing of the large amount of data produced.

In a typical gasification experiment, the coal is crushed to -4 +12 mesh, and a 5 to 20 g sample is placed in the reactor. The coal is then pyrolyzed at a heating rate of $3^\circ\text{C}/\text{min}$ in a flow of 1.0 to 2.5 l/min 20% hydrogen in nitrogen. System pressure during pyrolysis is 790 kPa (100 psig). The final pyrolysis temperature is that at which the gasification experiment is to be carried out. When the final pyrolysis temperature is reached, the reactor is flushed with nitrogen at the final temperature for approximately 30 min, and then steam and/or other reactants are introduced.

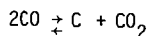
The product gas composition data are converted to rates of carbon conversion, which are then integrated over time to calculate the extent of carbon conversion. Rates and extents of carbon conversion are expressed on an ash-free basis. Following each gasification experiment the char residue in the reactor is burned to determine the final carbon balance for the experiment. Generally, carbon balances are near 100%.

RESULTS AND DISCUSSION

1. Steam-Char Reaction

The product gas from underground gasification consists primarily of hydrogen, carbon monoxide, carbon dioxide, methane, and nitrogen. This mixture constitutes a reducing atmosphere which sweeps through the coal during pyrolysis. In order to obtain a true simulation of these conditions during pyrolysis prior to our study of gasification kinetics, the sweeping gas mixture should contain all of these constituents.

However, the addition of carbon monoxide to the pyrolysis sweeping gas would result in the deposition of carbon, which would be added to the char in the gasification reactor. This additional carbon would be a product of the reverse Boudouard reaction, catalyzed by the coal ash and by the metal components of the reactor:



Deposited carbon is not quantitatively determinable and must be eliminated or made negligible in order to obtain a carbon balance. Therefore, our pyrolysis reactions have been carried out in a reducing atmosphere consisting of only hydrogen and nitrogen. Our experiments indicate that for Wyodak coal, pyrolysis in a reducing atmosphere (20% H_2 , balance N_2) results in recovery of approximately ten percent less char following pyrolysis than when pure nitrogen is used as the sweeping gas. However, the reactivity of the char produced in hydrogen and nitrogen is the same as that for char produced in pure nitrogen.

The rate of reaction of steam with chars prepared from Wyodak coal has been measured in the temperature range, 600-775°C, with a partial pressure of steam of 0.25-0.26 MPa (2.5-2.6 atm), and a total pressure of approximately 0.9 MPa (9 atm). These rates are plotted as a function of reciprocal temperature (Arrhenius plot) for Wyodak coal in Fig. 2. At each temperature, the reaction rates following gasification of 10% of the carbon and also following gasification of 50% of the carbon are shown. The rate at 10% carbon conversion corresponds to the rate for fresh char; the rate at 50% conversion corresponds to that for the more refractory residual char.

The apparent activation energies (E_a) calculated from Fig. 2 are summarized in Table 1. The decrease in E_a as a result of increasing the temperatures is much greater at 10% conversion than at 50% conversion, which is consistent with the expectation that micropore diffusion is a limiting factor for the steam-char reaction under conditions expected in an underground gasifier. By the time 50 percent of the carbon has been gasified, the micropore structure has opened somewhat, resulting in the higher values for E_a at 50% conversion.

Table 1
Apparent Activation Energies for Steam-Char Reaction

	E_a at 10% Conversion	E_a at 50% Conversion
Wyodak		
600°C	182 kJ/mol (43.6 kcal/mol)	235 kJ/mol (56.3 kcal/mol)
775°C	53 kJ/mol (12.8 kcal/mol)	109 kJ/mol (26.1 kcal/mol)
Hanna		
600°C	143 kJ/mol (34.1 kcal/mol)	156 kJ/mol (37.2 kcal/mol)
775°C	89 kJ/mol (21.2 kcal/mol)	110 kJ/mol (26.2 kcal/mol)

In Fig. 3, the temperature dependence of the rate of reaction of steam with chars prepared from Hanna No. 1 coal is shown. The steam partial pressure was 0.25 MPa (2.5 atm). The temperature range was 600-775°C. The apparent activation energies calculated from the curves for Hanna coal are also listed in Table 1. The lower values of E_a at higher temperatures for the Hanna coal are indicative of more severe micropore diffusion limitations with the Hanna char than with the Wyodak coal.

The Wyodak char pyrolyzed under simulated UCG conditions has a nitrogen BET surface area of approximately 1 m²/g, and the surface area measured by carbon dioxide adsorption is approximately 450 m²/gm. For the Hanna char, the BET surface is 0.2 m²/g, and the CO₂ surface area is approximately 550 m²/g. These data indicate that for both chars, the pore structure of the fresh char is limited to extremely small micropores. The pore structure of the Hanna char, as indicated by CO₂ surface areas, is apparently even smaller on the average than is that for the Wyodak char, an observation consistent with variations encountered in E_a for the steam-char reaction of each of these two chars. The micropores are apparently not accessible to the reactant steam, and must be opened appreciably to attain maximum reaction rates.

Wyodak chars prepared by pyrolysis at 3°C/min in either nitrogen or 20% H₂ in nitrogen were gasified at 700°C with steam at partial pressures of 0.12-0.65 MPa (1.2-6.5 atm). Reaction rate for Wyodak char is plotted as a function of steam partial pressure in Fig. 4. At lower partial pressures of steam, the curve is nearly linear, with a slope of approximately 0.85. This corresponds to a reaction order of 0.85 with respect to steam. At higher steam partial pressures, the reaction order decreases as indicated by the flattening of the curve in Fig. 4. Since underground gasification of coal would generally involve partial pressures of steam at the lower end of this range, the reaction order of 0.85 is probably applicable for use in the mathematical models proposed for this process.

Fig. 5 shows the dependence of the reaction rate on the partial pressure of steam for Hanna char. The reaction rate is plotted for conversions of 10, 30, and 50% of carbon, in the range of 0.1-0.27 MPa (1.07-2.7 atm) steam. In the case of the Hanna char, a series of parallel straight lines can be fitted through the points for the three extents of carbon conversion. The slope of these straight lines corresponds to a reaction order of 0.56 with respect to steam. This value is considerable lower than that obtained for the Wyodak char--undoubtedly due to diffusion of steam being limited by the finer pore structure of the Hanna char.

All gasification runs described up to this point were designed to maintain the partial pressures of product gases at values as low as possible. In runs with very high gasification rates (*e.g.*, at high temperatures or high partial pressures of steam) hydrogen levels were 2-4 mol %. However, in the majority of the runs, hydrogen content of the product was considerably less than 1 mol %. In order to investigate inhibition of the steam-char reaction by product hydrogen, a series of experiments was carried out in which hydrogen was added to the reactant steam. The range of hydrogen partial pressures investigated includes those expected to be encountered in the current low-pressure underground field tests (*i.e.*, up to approximately 0.1 MPa (1 atm)).

In Figs. 6 and 7 are shown the inhibitive effects of hydrogen at 600 and 700°C for Wyodak char. At 600°C (Fig. 6), inhibition of the reaction by hydrogen results in a rapid decline in reaction rate as the char is consumed. At 700° (Fig. 7), this inhibition is sufficient to eliminate the effects of diffusion limitations during the early stages of the reaction. At yet higher temperatures, the diffusion limitations are severe enough that they are apparent even in the presence of 0.75 atm hydrogen. At all temperatures, the higher the partial pressure of hydrogen, the earlier in the reaction that the rapid decrease in the reaction rate occurs. Hydrogen exerts a greater inhibitory effect at higher temperatures and as the extent of gasification increases. Similar effects of hydrogen have been observed with the Hanna coal.

2. Catalysis by Coal Ash

Many coals which would be good candidates of UCG have too high an ash content for economical aboveground utilization. This ash would be expected to have a catalytic effect on gasification reactions occurring underground. The ash in Hanna coal has been found to catalyze the water gas shift reaction and the methanation reaction under the conditions expected in UCG.

To investigate reaction 4), the water gas shift reaction, a series of experiments was carried out in which carbon monoxide and steam were reacted at various temperatures over a bed of char prepared from Hanna coal in the following manner. The char was prepared by heating to a temperature of 600°C at a heating rate of 3°C/min. This pyrolysis was carried out in a reducing gas mixture consisting of 20% H₂ in nitrogen. The overall pressure was 0.76 MPa (100 psig). The temperature was limited to 600°C during pyrolysis in order to minimize chemical changes that might occur in the mineral matter of the coal. On the other hand, at 600°C, most of the hydrocarbon decomposition would have occurred, yielding a clean, relatively hydrocarbon-free char to expose to the steam utilized for the reaction study.

Following pyrolysis, the temperature was reduced to the desired value and 0.13 MPa (1.33 atm) steam was introduced to the reactor along with 60 kPa (0.6 atm) carbon monoxide. The balance of the gas was nitrogen, and the total system pressure was 0.76 MPa (7.6 atm). The contact time of the gas mixture in the char bed ranged from 1.1 s at 500°C to 1.6 s at 250°C. Following utilization of the fresh char, 15% of the carbon was steam-gasified away at 600°C and then the shift reaction was studied at the lower temperatures. The purpose of the gasification step was to expose more of the mineral matter at the surface of the char particles. After the shift reaction rates were measured for the char from which 15% of the carbon had been removed, an additional 6% of the char was steam-gasified and the shift rates were measured again.

The results of these studies are shown in Fig. 8. The rates for the shift reaction over fresh char are appreciably lower than for the partially gasified char, but there is little difference between the rates obtained after 15 and after 21% carbon removal. In Fig. 8, the extent of the shift reaction as a function of temperature is compared with the thermodynamic equilibrium curve. Once an appreciable amount of the carbon has been gasified from the char, the reaction approaches thermodynamic equilibrium in the temperature range of 500 to 600°C. The point plotted for Wyodak char at 650°C was calculated from data obtained in an earlier gasification run in which carbon monoxide was observed in the product gas, permitting calculation of an equilibrium value. This point confirms that the reaction is indeed at equilibrium at 650°C, for a contact time on the order of one second.

At expected UCG processing condition, steam has been found to exhibit a synergistic effect with hydrogen for the production of methane. At 700°C, a mixture of 138 kPa (20 psig) hydrogen and 0.33 MPa (3.3 atm) steam was passed over Hanna char and yielded a methane concentration of 300 parts per million (by volume). Reaction at that partial pressure of hydrogen alone gave a methane concentration of only 150 ppm. Since this experiment was carried out under differential conditions, the hydrogen contributed by the steam-carbon reaction did not change the partial pressure of hydrogen in the reactor. Introduction of steam at 0.5 MPa (5 atm) gave a five-fold increase in the rate of methane production.

A probable mechanism for this phenomenon is methanation of the carbon monoxide produced by the steam-carbon reaction, with the methanation catalyzed by the mineral matter in the coal. The methanation of carbon monoxide by hydrogen has been found to occur when only the ash from Hanna coal (formed by low-temperature ashing) is placed in the reactor in the temperature range of 400 to 700°C. Insufficient experiments have been carried out to determine conversion rates for this reaction quantitatively.

3. Brackish Water Effects

The water occurring in the aquifers in the Hanna, Wyoming, area is quite brackish. A typical analysis is 600 mg/L sodium, 7 mg/L potassium, 22 mg/L calcium plus magnesium, 1100 mg/L carbonates, 400 mg/L sulfate, 40 mg/L chloride, and a pH of 8.5. There have been numerous reports in the literature that impregnation of coal with alkali or alkaline earth cations sometimes enhances the rates of gasification reactions with coal. Hence the inevitable use of brackish water in UCG may in fact enhance the kinetics of the steam-char reaction.

In a series of experiments to investigate this question, two aqueous solutions were prepared to simulate the brackish water characteristic of the water found in the Hanna aquifers. One solution containing approximately the natural concentrations of contaminants was prepared using calcium chloride, sodium sulfate, potassium carbonate and sodium bicarbonate. The second solution contained about five times the natural concentrations.

A sample of Hanna No. 1 coal was crushed and washed with boiling distilled water several times to remove any soluble salts already in the coal. A portion of this washed coal was gasified to obtain a base-line reaction rate. Ten grams of this washed coal was oven-dried and then impregnated with 1.0 ml of the simulated brackish water solution. The coal completely absorbed this solution; no excess liquid drained off. Likewise, a sample of the washed coal was dried, then impregnated with the solution having a fivefold concentration of contaminants. Each of these impregnated coal samples was then pyrolyzed and gasified.

Our standard gasification reaction conditions were used, i.e., 700°C, 0.25 MPa (2.5 atm) steam after pyrolysis had been carried out in 20% H₂/80% N₂ with a heating rate of 3°C/min to reaction temperature. The results of these runs are summarized in Fig. 9. Impregnation of the washed coal with the simulated brackish water appears to enhance the rate of reaction of steam with the char by ten to fifteen percent. There was little apparent difference between the effects of the standard concentration and the five-fold concentration of contaminants. An enhancement of the reaction rate of this small magnitude may not be significant because of the very small samples of coal gasified in each run. Normal variations in the coal can give this much variance in a measured reaction rate. The fact that the single-fold and the five-fold concentrations show little difference also suggests that the observed enhancement may not be significant.

Brackish water would be expected to have minimal effects on the reaction rate for a coal having the characteristics of Hanna No. 1. The core sample of Hanna coal which we are studying contains 17% ash, on an as-received basis. This means that the char remaining after pyrolysis contains 32% ash. The amount of inorganic material added to a coal with this high an ash content--even by using simulated brackish water having five times the normal concentration of contaminants--would be a rather small percentage of the total inorganic matter in the coal. Nevertheless, the possibility exists that brackish water may have an effect on the rate of reaction of steam with chars that have a lower ash content than does Hanna.

CONCLUSIONS

At high temperatures (700-750°C), the Wyodak char is 50-100% more reactive with steam than is Hanna char, although at lower temperatures (600-650°C), the two have essentially equal reactivities with steam. The lower apparent activation energy observed for the Hanna char indicates that its average pore size is smaller than that of the Wyodak char. The reaction order with respect to steam is greater for the Wyodak char than for the Hanna chars--undoubtedly also because of the differences in pore structure.

Hydrogen severely inhibits the reaction of steam with both chars. The inhibition is greater as a greater fraction of the carbon is gasified.

Mineral matter catalyzes the water gas shift reaction, and thermodynamic equilibrium is reached at approximately 550°C. The ash alone also has been found to catalyze the methanation reactions, but kinetic data have not yet been determined for these reactions.

The alkali and alkaline earth cations present in brackish waters exert a minimal catalytic effect on the steam-char reaction--most likely because the high ash content of the coal already supplies sufficient catalyst for the reaction.

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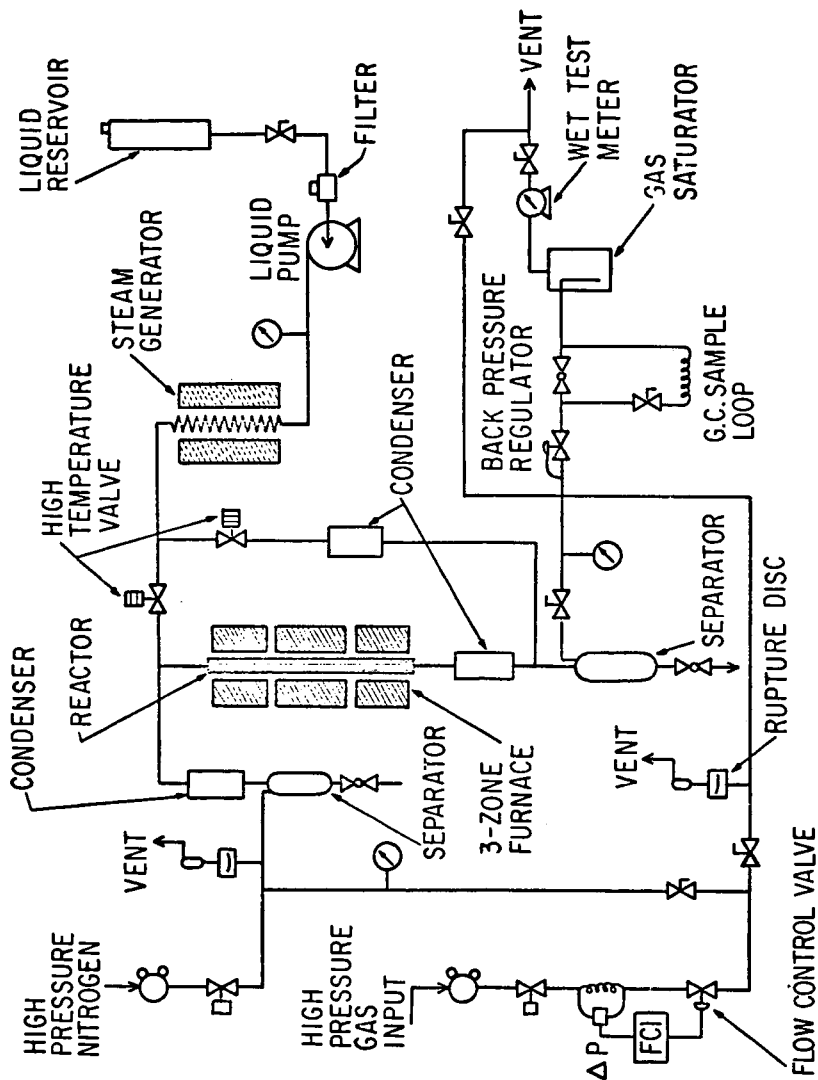


Fig. 1. Schematic of Char Gasification System

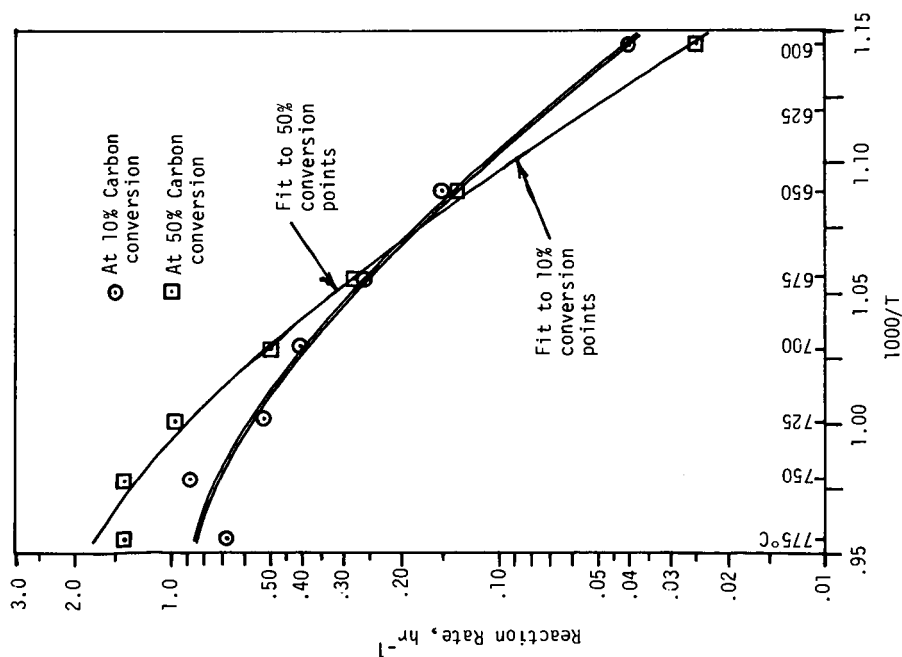


Fig. 2. Temperature Dependence of Steam-Char Reaction Rate. Wyodak Char, 0.25 MPa (2.5 atm) Steam

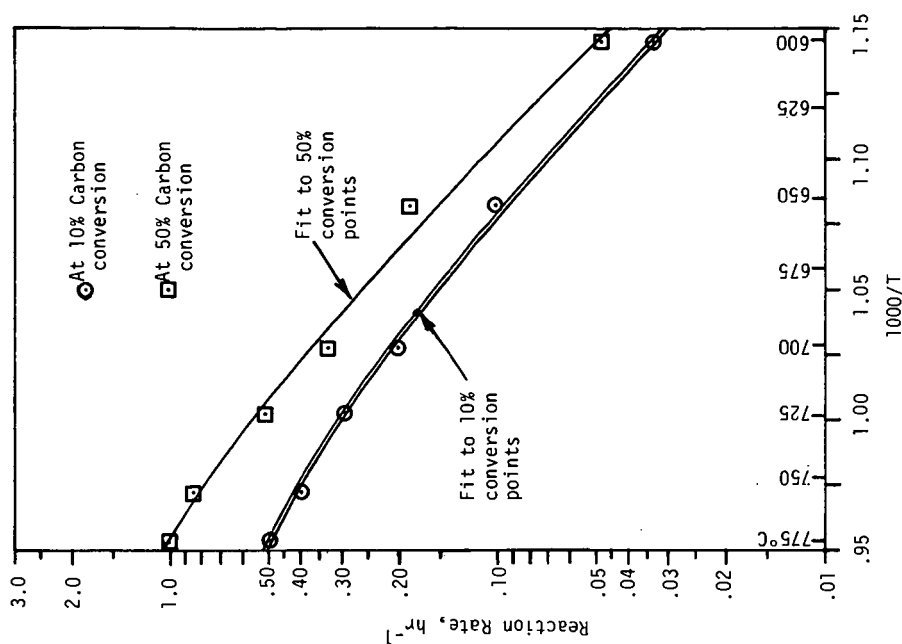


Fig. 3. Temperature Dependence of Steam-Char Reaction Rate. Hanna No. 1, 0.25-MPa (2.5-atm) Steam

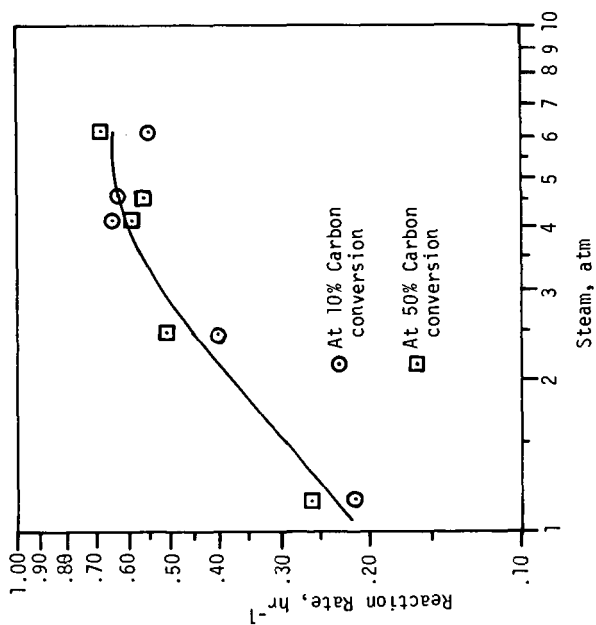


Fig. 4. Dependence of the Steam-Char Reaction Rate on the Partial Pressure of Steam. Wyodak Char, 700°C

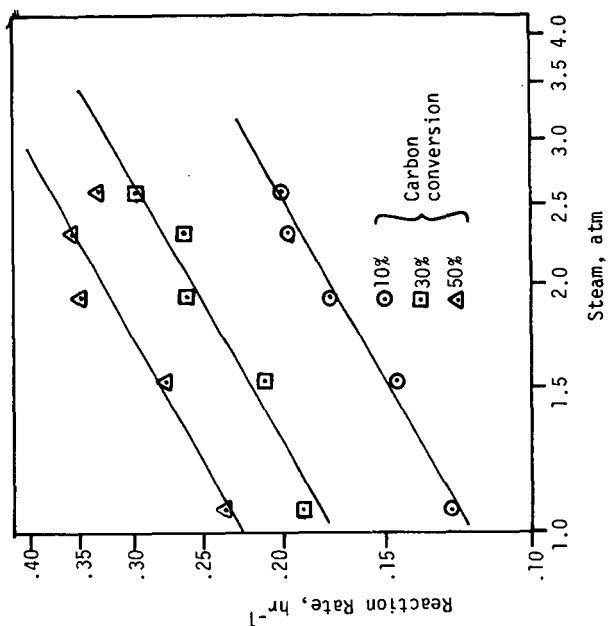


Fig. 5. Dependence of the Steam-Char Reaction Rate on the Partial Pressure of Steam. Hanna No. 1 Char, 700°C

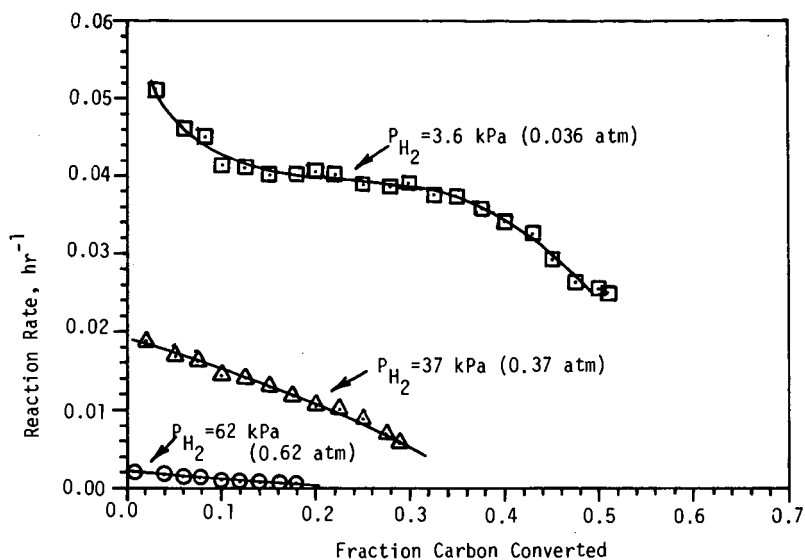


Fig. 6. Hydrogen Inhibition of the Steam-Char Reaction.
Wyodak Char, 600°C, 0.25 MPa (2.5 atm) Steam

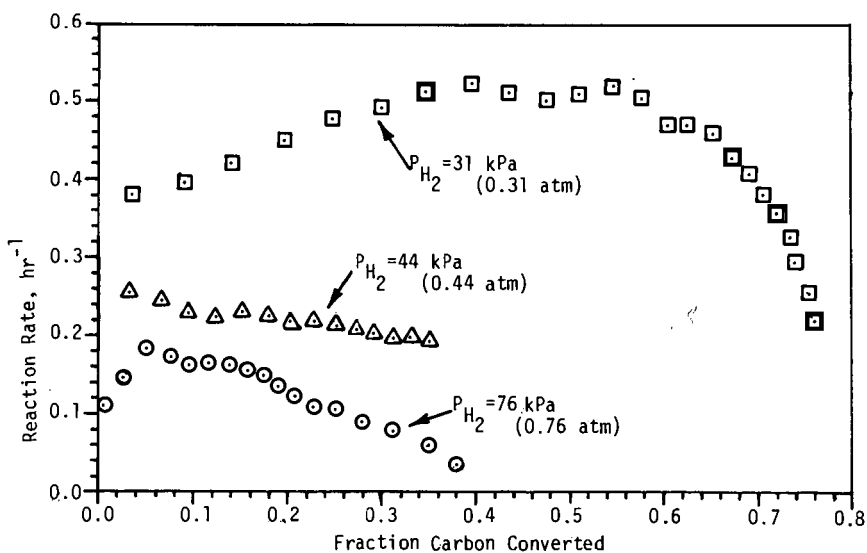


Fig. 7. Hydrogen Inhibition of the Steam-Char Reaction.
Wyodak Char, 700°C, 0.25 MPa (2.5 atm) Steam

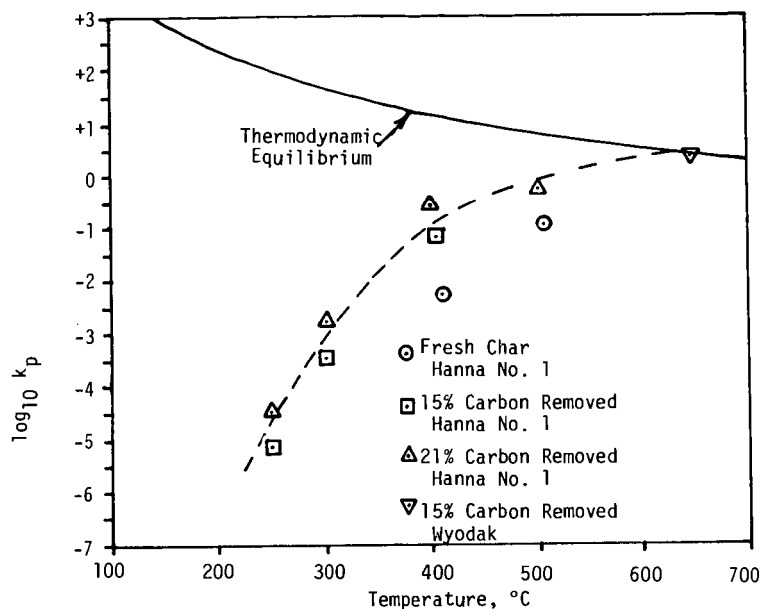


Fig. 8. Water Gas Shift Reaction. 1.0-1.5 s Contact Time

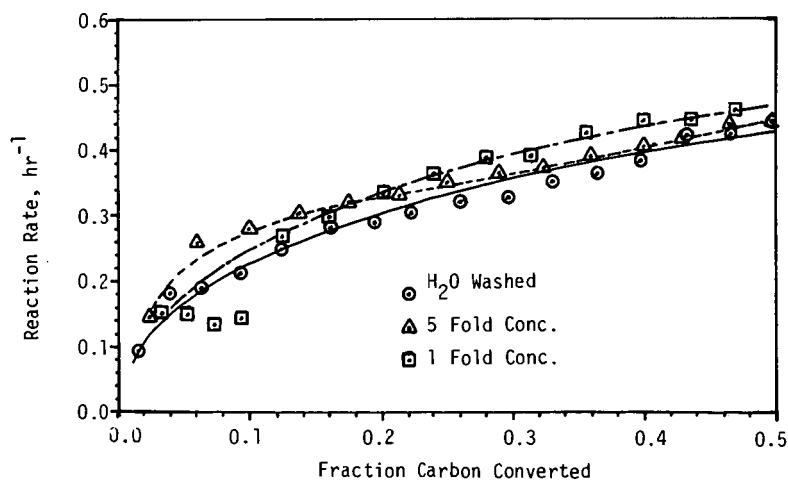


Fig. 9. Effect of Brackish Water on Steam/Char Gasification Rate. Hanna No. 1 Char, 700°C , 0.25 MPa (2.5 atm) Steam